RESEARCH ARTICLE

Synthesis and Characterization of Proton Conducting Polymer Electrolytes based on Poly (N-vinyl pyrrolidone) and Polyvinylchloride

C. Latha

Siri PSG Arts and Science College for Women, Sangagiri, Tamil Nadu, India

ABSTRACT: Poly (N-vinyl pyrrolidone) (PVP), Polyvinylchloride (PVC) blend membrane doped with different molar weight percentage of NH4Br has been prepared by solution casting technique using dimethyleformamide (DMF) as solvent and characterized for electrical properties. The prepared polymer electrolyte has been studied by XRD, FT-IR, Dielectric and Capacitance measurements. The XRD results show that the amorphous nature of PVP has increased in 70%PVP: 30%PVC. It is also observed that the amorphous nature of 70%PVP: 30%PVC is further increased by the addition of different concentration of NH4Br. A complex formation of PVP: PVC, PVP: PVC: NH4Br have been confirmed by FT-IR studies. Proton conductivity for the above film has been measured using impedance spectroscopy. The polymer blends 70%PVP: 30%PVC shows an ionic conductivity of 8.46X10-8 Scm-1. The conductivity of the blend film increases as concentration of NH4Br increases. The maximum proton conductivity 2.78X10-3 Scm-1 has been observed for 70%PVP: 30%PVC: 0.6 Molar weights (MWt) NH4Br. The primary proton battery with configuration of Zn + ZnSO4.7H2O/70PVP:30PVC: 0.6 Mwt% NH4Br/PbO2 + V2O5 are fabricated and tested.

KEYWORDS: PVP, Proton conducting, DMF, conductivity analysis, XRD, FT-IR

https://doi.org/10.29294/IJASE.8.1.2021.2099-2105 **©2021Mahendrapublications.com, All rights reserved**

1. INTRODUCTION

Solid state Ionics is a thrust area of research in the branch of materials science, deals mainly with the solid materials which exhibit rapid / fast ion transport through the bulk. The ionic conductivity of these solids is exceptionally high and comparable to that of liquid /aqueous electrolytes. Hence they can be potentially used as excellent alternates of liquid/aqueous electrolytes to fabricate solid state electrochemical devices viz. batteries. The research in the field of solid state Ionics encompasses investigations of physical and chemical behaviour of solids with fast ion movement within the bulk as well as their technological aspects. These materials widely referred to as 'Super ionic Solids' or 'Solid Electrolytes' or 'Fast Ion Conductors' show tremendous scope to develop all-solid-state mini/micro electrochemical devices viz. batteries, fuel cells, super capacitors, electro chromic displays, sensors, photo electrochemical solar cells (PESCs) etc [1].

Over the past ten years, spectacular development has been seen in micro electronics industry but till date the application of integral power sources has not been realized. The development of new types of electrical power generators and storage systems are quite essential for further integration of the electronic industry. The self-contained power source is a growing trend in numerous fields such as pocket calculators, bio-medical devices, cameras and electronic watches [2]. The presently available conventional battery system contains a liquid electrolyte generally a concentrated aqueous solution of potassium hydride or sulphuric acid. This liquid electrolyte has high ionic conductivity and offers very good contact with electrodes. But the major problems associated with liquid electrolytes are cell leakage corrosion self-discharge process drying out of the cell loss of electrolyte and severe restrictions on the capability of useful discharge at very low temperatures [3]. The significant advantages of polymer blends are that the properties of the final product can be tailored to the requirement of application, which cannot achieved alone by one polymer. However, the film properties depend on the miscibility of blend. The polymer-polymer miscibility may arise from any one of the interactions such as hydrogen bonding, dipole-dipole forces and charge transfer complexes for homo polymer mixtures [4-7].

In the present study, we describe the method of synthesis of proton conducting polymer. The samples were characterized using X-ray

**Corresponding Author: lathaphysics26@gmail.com*
Received: 13.06.2021 **Accepted:** 25.07.2021 **Published on**: 02.08.2021

Diffraction (XRD) technique, Fourier Transform Infrared (FT-IR) technique, Dielectric studies and Capacitance measurements.

2. EXPERIMENTAL METHODS

Pure PVP sample and the samples of PVP with PVC were mixed in the molar ratio; 70:30 have been prepared by solution cast technique using DMF as the solvent. The conductivity has been studied for the above films. From the above compositions 70:30ratios have better conductivity. Hence 70%PVP: 30%PVC have been chosen for this study. Films of pure PVP, 70%PVP: 30%PVC and films of 70%PVP: 30%PVC with ammonium bromide in the molar ratios 0.6Mwt% have been prepared by solution cast technique using DMF as solvent. The solutions of PVP, PVC and with ammonium bromide were stirred well for 10–12 h to obtain a homogeneous solution and then cast on to polypropylene dishes and evaporated slowly at room temperature. Figure.1 shows the schematic representation of different steps involved in the solution cast technique.

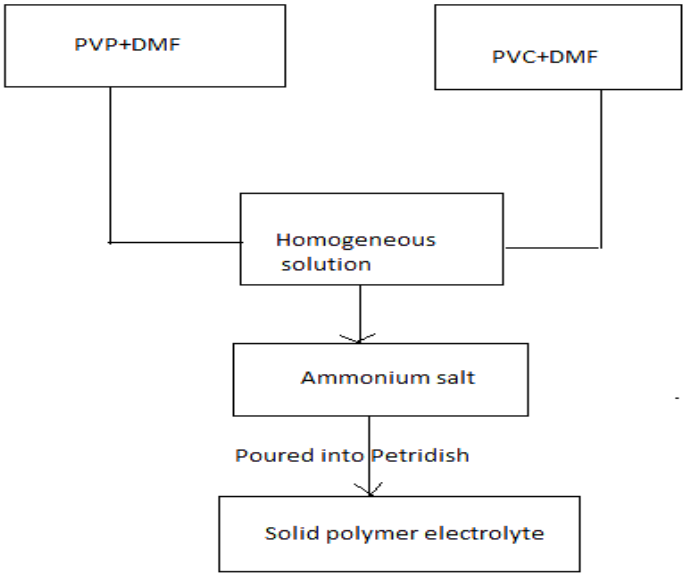

Figure 1. Schematic representation of different steps involved in the solution cast technique

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

Fig.2 shows the XRD pattern of pure PVP, 70%PVP: 30%PVC and 70%PVP: 30%PVC doped with NH_4Br having mole ratios. It has been observed from Fig (2a), the broad peaks between 12–15^0 and 19–24^0 associated with the amorphous nature of pure PVP [8]. The relative intensity of the broad peaks decreased by adding 30% PVC (Fig 2b), Fig. (2c), shows the addition of 0.54Mwt% of NH_4Br to the blend polymer the amorphous nature are slightly modified and some crystalline peaks of 20-23^0 are obtained, in which a maximum diffusivity of salt of NH_4Br with blend polymer matrix [9]. These peaks are recognized as the recrystallization of ammonium bromide of the film surface.

3.2. FT-IR Analysis

FT-IR spectrum has been widely used to study the interaction between cations, anions, solvent and polymers. The IR spectra of pure PVP, 70PVP:30PVC, blend with 0.6%Mwt% of NH_4Br are shown in Figure 3. It may be observed from Fig.3a, in the case of pure PVP, the observed band around 542 cm^{-1} has been attributed to C-Br stretching, the band observed at 640 cm^{-1} has been attributed to O-N stretching, the C–H Bending peak observed at 846 cm^{-1}, the observed band around 1220 cm^{-1} has been attributed to C-O stretching, C=O stretching has been observed at 1673 cm^{-1}.

Fig.3b shows that in the combination 70%PVP: 30%PVC, the observed C-Br stretching peak is shifted from 542 $cm^{-1}$to 556 cm^{-1}, C–H bending peak observed at 846 cm^{-1}, the band at 1218 cm^{-1} attributed to C-O stretching and C=O stretching has been observed at 1634 cm^{-1}. The observed shift may be due to the interaction of PVP and PVC. Fig 3c shows the FT-IR spectra of 70%PVP: 30%PVC: 0.6wt% of NH_4Br. From the Figure it can be seen that the C-Br stretching peak is shifted to 536 cm^{-1}, C–H Bending peak observed at 887 cm^{-1}, the band at 1272 cm^{-1} attributed to C-O stretching

for O-N stretch. The observed shift is due to interaction of PVP, PVC and ammonium bromide.

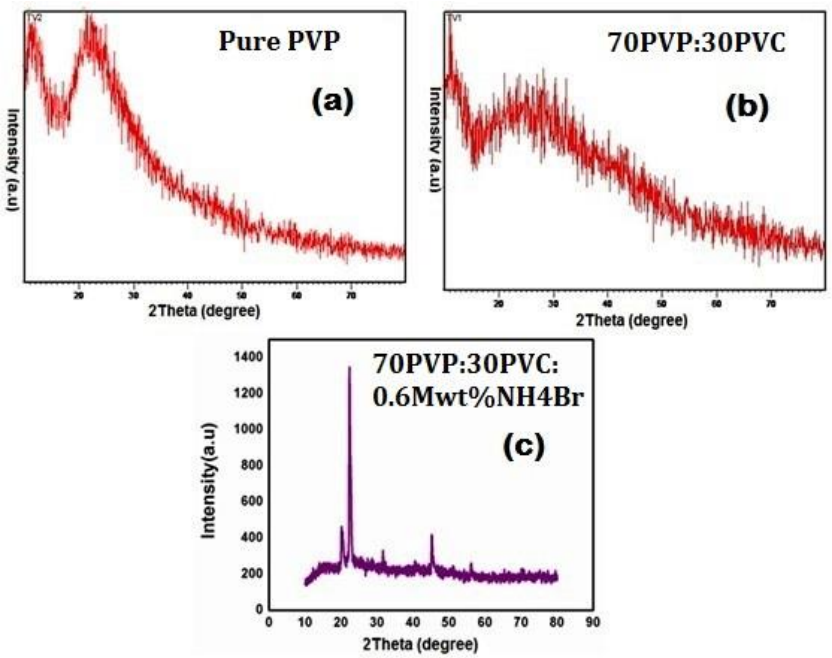

Figure 2. (a) XRD pattern of pure PVP,(b)70%PVP: 30%PVC, (c)70%PVP 30%PVC: 0.6 Mwt% of NH_4Br

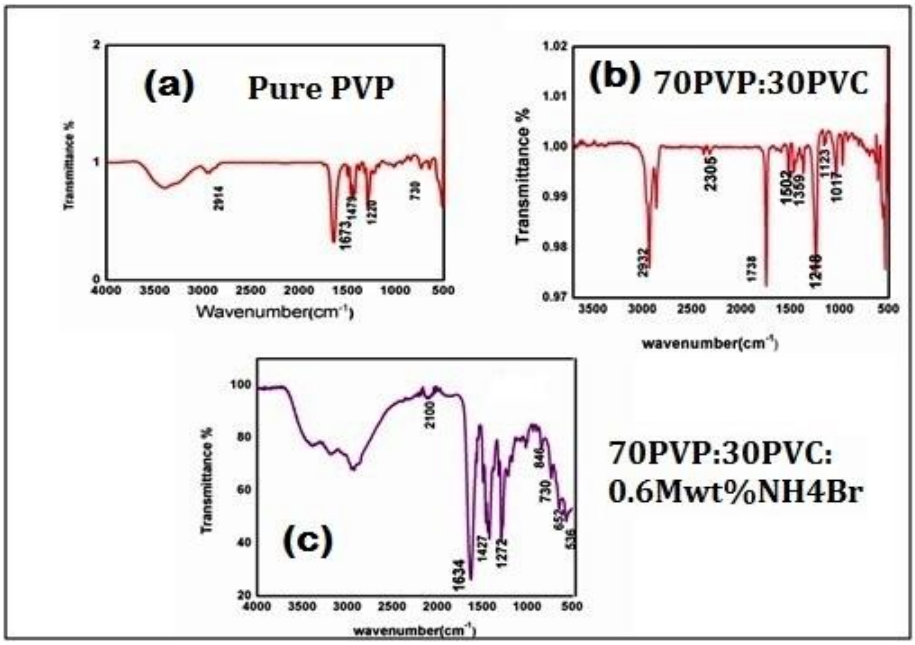

Figure 3. FT-IR (a) Pure PVP, (b)PVP: PVC, (c)PVP: PVC: NH_4Br

Table 1: FT-IR assignment for pure PVP, 70%PVP: 30%PVC and 70%PVP: 30%PVC: 0.6wt%NH_4Br

Wavenumber cm^{-1} Pure PVP	70%PVP:30%PVC	70%PVP:30%PVC:0.6M wt% of NH_4Br	Assignments
542	556	536	C-Br stretch
640	644	-	O-N stretch
846	887	846	C-H bend
1220	1218	1272	C-O stretch
1673	1634	-	C=O stretch

3.3 Conductivity Studies

Fig. 4 shows the frequency dependent on the conductivity of pure PVP, 70%PVP: 30%PVC, 70%PVP: 30%PVC: 0.6Mwt%NH_4Br polymer electrolyte at room temperature. From the figure, it can be seen that the conductivity increases with increasing of ammonium salt. The pure PVP shows higher conductivity than 70%PVP:30%PVC blend electrolyte because of PVC has crystalline nature [11]. When ammonium bromide is added to the blend, the conductivity increases and shows maximum high ionic conductivity $2.78x10^{-3}Scm^{-1}$for 70%PVP: 30%PVC: 0.6Mwt% NH_4Br. As reported earlier, at low salt concentration the ionic conductivity of solid polymer electrolytes increases due to the accumulation of charge carriers. At high salt concentrations, the conductivity decreases due to build-up of charge carriers offset by the retarding effect of ion cloud [10].

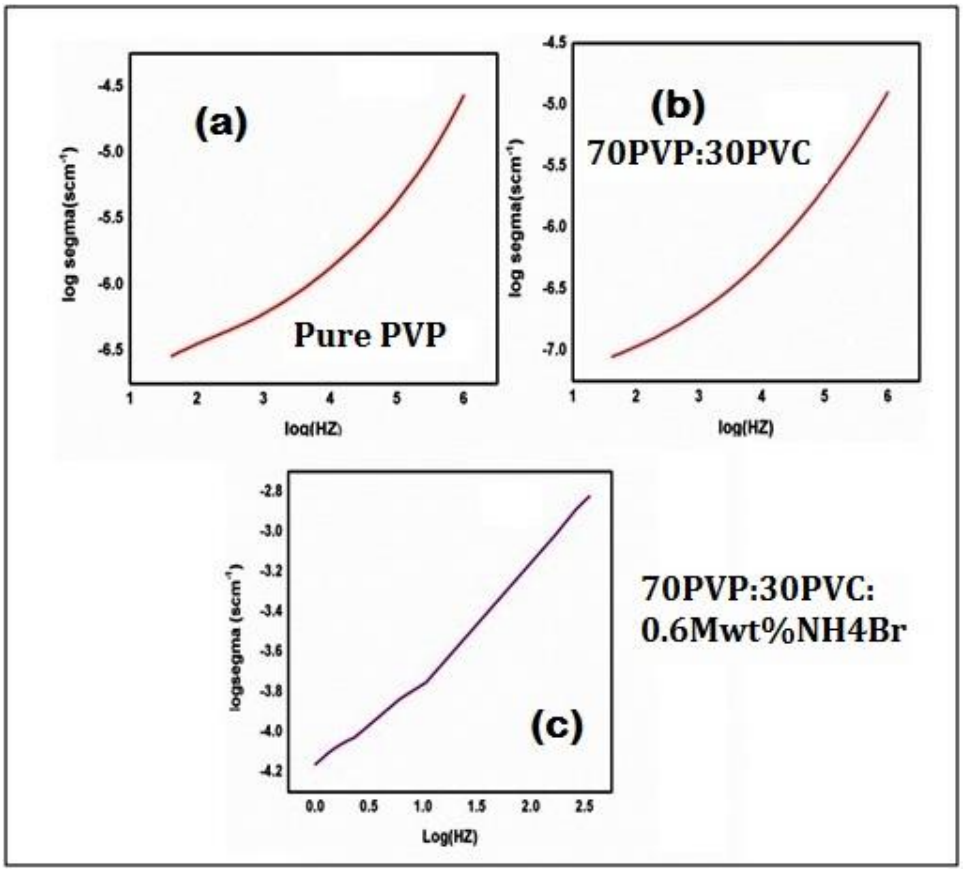

Figure 4. Conductance spectra of pure PVP (a), 70PVP: 30PVC (b) 70PVP: 30PVC:0.6 Mwt% NH_4Br (c)

Table (2): Ionic conductivity values of (a) Pure PVP, (b) 70%PVP:30%PVC, (c) 70%PVP: 30%PVC: 0.6Mwt% of NH_4Br

S.No	Polymer complexes	Ionic conductivity
1	Pure PVP	$3.72x10^{-7}Scm^{-1}$
2	70%PVP:30%PVC	$8.47x10^{-8}$ Scm^{-1}
3	70%PVP:30%PVC: 0.6Mwt% of NH_4Br	$2.78x10^{-3}$ Scm^{-1}

3.4 Dielectric Constant (Ɛ')

Fig.5 shows the variation of dielectric constant versus frequency. The dielectric constant decreases with increasing of frequency. High values of ε´ are due to the interfacial effect within the bulk of the sample and the electrode effects [12]. The dielectric constant is inversely proportional to the frequency. This is a normal dielectric behavior that the dielectric constant decreases with an increase in frequency. This is due to the mechanism of polarization [14].The large value of Ɛ′ is also due to the motion of free charge carriers within the material [15]. Higher values have been explained by the presence of space charge effects, contributed by the accumulation of charge carriers near the electrodes [16]. In pure PVP, the dielectric constant is not zero at high frequency ($1x10^5$), but when PVC is added to pure PVP, the dielectric constant attains zero. Addition of NH_4Br in the ratio 0.6Mwt% to 70%PVP: 30%PVC, the dielectric constant increases with decreasing frequency [17]. This help to increase the motion of ammonium ions between the electrodes

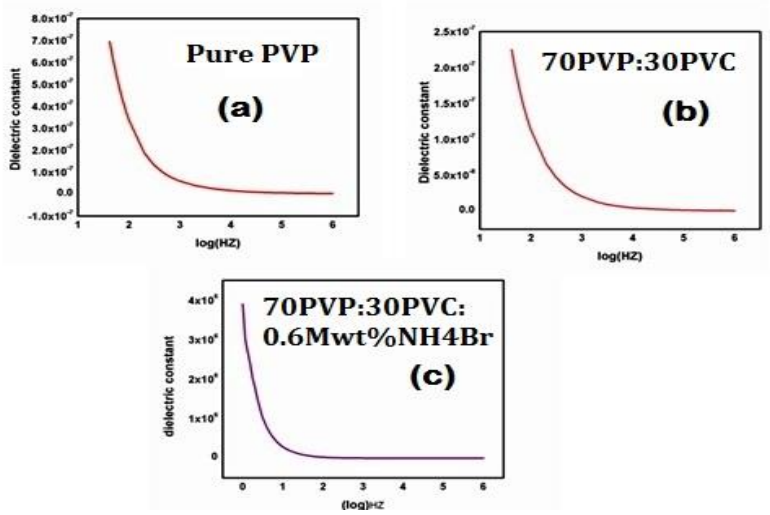

Figure 5. Variation of Dielectric constant versus frequency

3.5 Capacitance versus frequency

The capacitance value increases at low frequency when adding NH_4Br in the ratio of 0.6Mwt% to 70%PVP: 30%PVC. The capacitance value decreasing with increasing frequency comparing pure and blend the capacitance value is constant when increasing the frequency, the capacitance value is increase at low frequency because of large number of ionic movements [18].

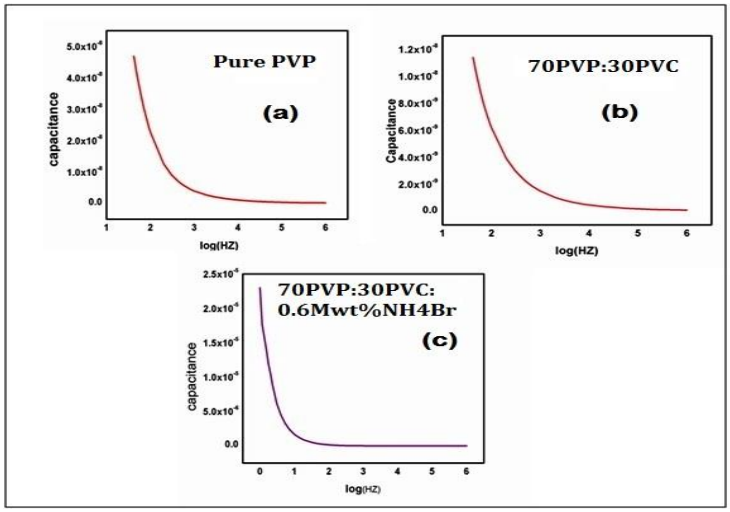

Figure 6. Variation of capacitance vs frequency 0.6 Mwt % of NH_4Br

3.6 Fabrication and characterization of primary proton battery

The highest conducting sample in the PVP: PVC: NH_4Br system is used as an electrolyte for battery fabrication. The preparation of the anode desired proportions (3:1:1) of zinc (metal) powder, $ZnSO4.7H_2O$ and graphite powder were taken and mixed together and finally grind well. Then, the mixture was pressed to form a thin pellet. The preparation of cathode the ratios are (8:2:1:0.5) PbO_2, V_2O_5, graphite and polymer electrolyte was taken and mixed together and finally grind well. The above mixture was made into thin pellet. Graphite C was added to introduce the electronic conductivity, while the addition of the polymer electrolyte helps in reducing the electrode polarization. The polymer electrolyte was sandwiched between the anode and cathode pellets. The open circuit voltage (OCV) of the cell was monitored for 60 h with configuration

Zn + $ZnSO_4.7H_2O$/70PVP:30PVC: 0.6 Mwt% NH_4Br/PbO_2 + V_2O_5.

The protonic oxidation takes place at the electrode-electrolyte interface and following reversible reaction takes place [19].

$$nZn + ZnSO_4.7H_2O \rightleftarrows Zn_{n+1}(SO_4).(7-2n)\,H_2O.2n(OH) + 2nH^+ + 2ne^-.$$

This confirms the proton (H^+ ion) conducting nature of the prepared polymer electrolyte. Further the NH_4^+ ion is responsible for the transport mechanism.

Cathode reactions

$$PbO_2 + 4H^+ + 2e^- \rightleftarrows Pb^{2+} + 2H_2O$$

$$V_2O_5 + 6H^+ + 2e^- \rightleftarrows 2VO^{2+} + 3H_2O.$$

The OCV of a proton cell is described as the difference between the equilibrium potentials at each electrode, with the positive and negative electrode potentials (Fig.7 battery holder).The stabilized voltage of 0.9 V observed for the cell is shown in Fig 8. The region in which the cell voltage remains constant is called as the ‘‘plateau region’’. Beyond the plateau region, voltage value of the cell drops. This is due to the activation polarization which occurs when the speed of an electro chemical reaction at an electrode surface is restricted by slow moving electrode kinetics [20].

CONCLUSION

Proton conducting polymer electrolytes based on poly (N-vinyl pyrrolidone) (PVP) and (PVC) and NH_4Br have been prepared by solution cast technique. The amorphous nature and crystalline nature of polymer electrolytes have been confirmed from the reduction in intensity and broad nature of XRD patterns of the polymer electrolyte. A complex formation of pure PVP, PVP: PVC, PVP: PVC: NH_4Br has been confirmed by FTIR studies. Proton conductivity is measured using conductivity studies. Pure polymer conductivity is 3.78 $x10^{-7}Scm^{-1}$. A doped blend polymer 70%PVP: 30% PVC shows an ionic conductivity is $8.46x10^{-8}$ Scm^{-1}.The conductivity of the blend film increases with increases of NH_4Br.The maximum proton conductivity of $2.78x10^{-3}$ Scm^{1} has been observed for 70%PVP: 30%PVC: 0.6Mwt% of NH_4Br. The optimized polymer electrolyte 70PVP:30PVC:0.6Mwt% NH_4Br possesses high conductivity, high amorphous nature and high capacitance nature is applied for proton battery and the stabilized voltage of the battery is reported.

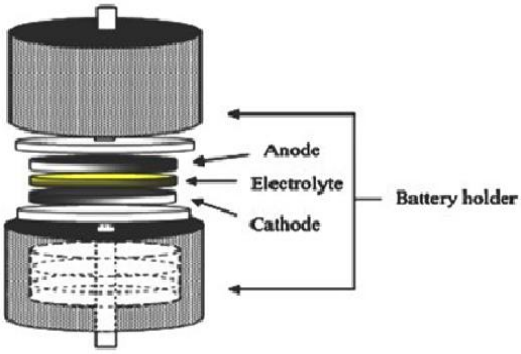

Figure 7. Battery holders

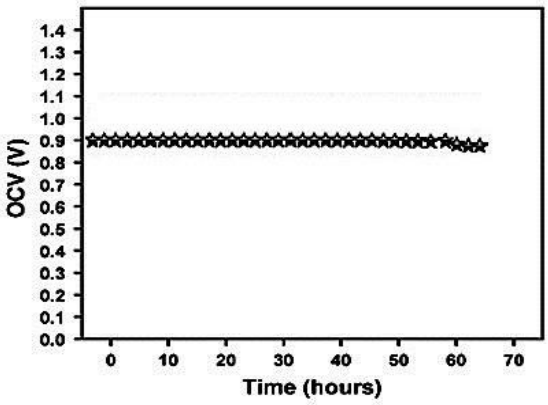

Figure 8. Open circuit voltage (OCV) as a function of time

REFERENCES

[1] Agrawal R.C, PandeyG. P, 2008. Solid polymer electrolytes: materials designing and all solid-state battery applications: an overview, Physics D: APPl. Phys. 41.

[2] MinamiT, TatsumisagoM., WakiharaM., IwakuraC., KohhuiyaS and Tanaka (eds) (2005). “Solid State Ionics for Batteries”, Springer – Verlag,Tokyo.

[3] Varnell DF, Cole man MM, 1981. FT-IR. Studies of polymer blends: Further observations onpolyester-poly (vinyl chloride) blends. Polymer22:1324-1328

[4] Coleman M.M, Zarin J.J, 1797, Fourier-transform infrared studies of polymer blends. II. Poly (ecaprolactone) – poly (vinyl chloride) system. PolymSci Polymer Phys Edn17, 837-850

[5] Garton A, Aubin M, Prudhomme RE, 1983. FTIR of polycaprolactone / poly (vinylidene chloride-co-acrylonitrile miscible blends, J Poly. SciPolym Lett Edn 21, 45-47.

[6] Varnell DF, Runt JP, Coleman MM, 1983. FTIR. and thermal analysis studies of blends of poly(ecaprolactone) with homo- and copolymers of poly(vinylidene chloride). Polymer 24, 37-42.

[7] Woo EM, Barlow JW, Paul Dr, 1986, D.R. Paul .J. 1986. Phase behavior of blends of aliphatic polyesters with avinylidene chloride/vinyl chloride copolymer. ApplPolymSci, 32, 3889-3897.

[8] Morita M., Arki F., Yoshimoto N.,IshikawaM, TsustsumiH., 2000. Solid State Ionics 136-137, 1167.

[9] Nishi T, Wang T.T, Kwei T.K, 1975. Thermally induced phase separation behavior of compatiblepolymer mixtures. Macro Mol8:227-234

[10] Latha C.,Venkatachalam K, (2016). Structural, Vibrational, Thermal, Electrical Properties of PVP - PVC blend NH_4SCN ,Polymer Bulletin 1874-1

[11] Anji Reddy Poln and Ranveerkumar, 2011. Bull Mater .Sci. 34, 1063-1067.

[12] Kothapalle, S., Koramala, N.K., Naresh, V. and Srinivasa, B. 2011. Structural and Optical Properties of Li+: PVP & Ag+: PVP Polymer Films.Material Sciences and Applications, 2, 1688-1696.

[13] Reddeppa Nadimicherl Sharma A. K., Narasimha Rao V. V. R., Wen Chen, 2014. AC Conduction mechanism and battery discharge characteristics of polybend films complexed with potassium chloride, Measurement 47, 33-41.

[14] Kumar M, Sekhon SS, 2002. Ionic conductance behaviour of plasticized polymer electrolytes containing different plasticizers. Ionics 8, 223–233.

[15] Sivaiah K, Kumar KN, Naresh V, Buddhudu S, 2011. Structural and optical properties of Li+: PVP & Ag +: PVP polymer films. Mater SciAppl 2, 1688–1696.

[16] Ramya CS, Selvasekarapandian S, Savitha T, Hirankumar G, Angelo PC 2007. Vibrational and impedance spectroscopic study on PVP-NH_4SCN based polymer electrolytes. Physica B 393, 11–17.

[17] Kyrtsis A, Pissis P, Grammatikakis J. 1995. Dielectric relaxation spectroscopy in poly(hydroxyethyl acrylates)/water hydrogels. J PolymSci Part B Polym Phys 33, 1737–1750.

[18] Saritha, Department of Physics National Institute of Technology Rourkela-769008

[19] Guitton J., Dongui B., Mosdale R., Forestier M, 1988. New negative metallic electrode for solid batteries with a solid protonic conductor (SC) as electrolyte, Solid State Ionics, 28-30,847-852.

[20] Ng L.S., Mohamad A.A, 2006. Protonic battery based on a plasticized chitosan-NH_4NO_3 solid polymer electrolyte. J. Power Sources, 163, 382-385.

All © 2020 are reserved by International Journal of Advanced Science and Engineering. This Journal is licensed under a Creative Commons Attribution-Non Commercial-ShareAlike 3.0 Unported License.